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Transformation toughening and grain size control in β''-Al_2O_3/ZrO_2 composites

D. J. GREEN*
Structural Ceramics Group, Rockwell International Science Center, 1049 Camino Dos Rios, Thousand Oaks, California 91360, USA

In order to fabricate transformation-toughened β''-Al_2O_3 and optimize its mechanical and electrical properties it was found to be necessary to carefully control the particle size distribution of the starting powders and their mixing. The ionic resistivity of the composites depended primarily on the volume fraction of ZrO_2. Additions between 10 and 20 vol% produced materials with ionic resistivities (300° C) between 6 and 10 Ωcm and eliminated exaggerated grain growth of the β''-Al_2O_3. Comparison of β''-Al_2O_3 composites containing either tetragonal (t-) ZrO_2 or cubic (c-) ZrO_2 with the single phase material showed that the major strengthening mechanism is the reduction in critical flaw size. This occurred by the elimination of the flaw population associated with abnormally large grains. For maximum increases in fracture toughness and strength, however, the use of t-ZrO_2 (transformation toughening) as a second phase is preferred.

1. Introduction

The concept of transformation toughening for ceramic materials is well established both theoretically and experimentally [1–3], and usually involves the retention of tetragonal ZrO_2 as a second phase in the material. The phase transformation, t-ZrO_2 to monoclinic (m-)ZrO_2, can be induced by stress and leads to an increase in fracture toughness [1–3]. The concept has been applied to several ceramic systems, including the ionic conductor Na β''-Al_2O_3 [4–6].

Single phase β''-Al_2O_3 is currently being used as a solid electrolyte in the development of the Na–S battery. The technical feasibility of this battery has been demonstrated but its lifetime is often limited by electrolyte degradation. Two failure modes have been identified [7] and analysis of one of these modes [8–10] indicates that the critical current density for initiation of failure should depend on fracture toughness. It is feasible, therefore, that improvements in fracture toughness, such as that offered by transformation toughening, has the potential to improve the reliability of the battery. Moreover, if the increases in fracture toughness can be translated into increases in strength, the mechanical reliability of the material would also be improved.

In the initial study of Lange *et al.* [4] it was shown that the addition of 15 vol% ZrO_2 to β''-Al_2O_3 gave average strengths ~350 MPa and K_{IC} values of ~4.5 MPa m$^{\frac{1}{2}}$. These mechanical properties are substantially higher than those of the single phase β''-Al_2O_3. Further increases in strength (up to 440 MPa) were obtained in a later study when agglomerates were removed from the starting powders [6]. There was, however, an associated increase in ionic resistivity and it was suggested by the authors that it may not be necessary to remove the β''-Al_2O_3 agglomerates from the powder, as this may reduce the final grain size of the β''-Al_2O_3 phase and hence give rise to a higher ionic resistivity. The increase in the fracture toughness with the addition of t-ZrO_2 to β''-Al_2O_3 has been associated with the transformation toughening mechanism [4–6] and this was substantiated by X-ray

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*Present address: 118 Steidle Building, The Pennsylvania State University, University Park, Pennsylvania 16802, USA.

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diffraction of fracture surfaces [6]. It was, however, pointed out by Green and Metcalf [6] that the strengthening in the composites is not simply a result of transformation toughening but also in the reduction of the critical flaw size. From microstructural observations it was found that additions of ZrO_2 ($\geqslant 10$ vol %) controls grain growth of the β''-Al_2O_3 phase and eliminates the formation of abnormally large grains. Thus, the ZrO_2 additions would remove any flaw populations associated with such large grains.

The aim of this study is to compare the mechanical properties and ionic resistivity of two sets of composites, one containing t-ZrO_2 and one containing c-ZrO_2. It was hoped that this would improve the understanding of the strengthening mechanisms in these materials, and in particular to indicate whether it was the reduction in critical flaw size or transformation toughening that was the major strengthening mechanism.

2. Experimental procedure

Commercial powders* of β''-Al_2O_3, ZrO_2 (2.4 mol % Y_2O_3) and ZrO_2 (6.6 mol % Y_2O_3) were obtained. The ZrO_2 powders were dispersed in water (pH 2.5) and allowed to sediment such that agglomerates $\geqslant 1\,\mu m$ had settled to the bottom of the container. The supernatant dispersion was then flocculated, washed several times with acetone, dried and calcined at 320° C. The β''-Al_2O_3 powder was dispersed in 1-butanol (~ 35 vol % solids) and was allowed to sediment for various times. The sedimentation times for all powders were calculated assuming Stokes Law to be valid. After pouring off the supernate from the β''-Al_2O_3 slip, the appropriate amount of ZrO_2 powder was added, such that the composites when fired would contain up to 25 vol % ZrO_2. The composite slip was mixed using an ultrasonic probe,† and cast into teflon moulds located on the top of plaster of paris forms. For strength testing specimens, the moulds were 50 mm × 50 mm and for fracture toughness or ionic conductivity specimens the moulds were 32 mm diameter. The green bodies were dried at ambient temperatures in a glove box (argon atmosphere) for at least 2 days. Green densities of specimens were typically in the range 50 to 60% theoretical density.

The specimens were sintered at 1535° C (1 h) in a covered, high purity Al_2O_3 crucible, containing a bed of β''-Al_2O_3 powder to minimize sodium loss. The densities of the fired specimens were determined by a volume displacement technique using neothene and were typically $> 97\%$ theoretical. The phases in the fired composites were determined by X-ray diffraction. In particular, the relative amounts of β and β''-Al_2O_3 were qualitatively assessed using a normalized index $f'(\beta)$. This index was calculated by forming the ratio of the integrated intensity of the $(2\,0\,6)\beta$ peak to the sum of the intensities of this peak and the $(0\,2, 1\,0)\beta''$ peak.

Specimens for the determination of the critical stress intensity factor (K_{IC}) and ionic conductivity were diamond machined and polished using $3\,\mu m$ diamond paste, with kerosene as a coolant and lubricant. K_{IC} values were determined using the indentation technique, originally developed by Evans and Charles [11] and refined by Evans [12]. The ionic conductivity was determined at 300° C for all composites and over the range 250 to 350° C for selected compositions. The conductivity values were obtained by measuring the a.c. impedance and phase angle across the specimens from 100 Hz to 100 kHz, using a multifrequency LCR meter.‡ The electrodes consisted of fibre glass filter paper into which an eutectic mixture of $NaNO_3/NaNO_2$ had been soaked. This cell was compressed between platinum foils to which platinum lead wires had been welded, placed in a crucible furnace and heated to 350° C. After equilibration of approximately 1 h, the furnace was slowly cooled until the selected temperature or temperatures were reached. To determine whether the ionic conductivity apparatus was functioning correctly, commercially available discs of β''-Al_2O_3§ were measured. After the completion of the electrical measurements, the specimens were thermally etched in a covered Al_2O_3 crucible (1500° C, 10 min) and viewed on the scanning microscope (SEM) to study the microstructure, particularly for the dispersion of the ZrO_2 and for microstructural defects.

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*β''-Al_2O_3, Ceramatec Inc, Salt Lake City, Utah, USA. ZrO_2, Zircar Inc, Florida, NY, USA.

†Fisher Sonic Dismembrator Model 300.

‡Hewlett Packard, Model HP 4274A.

§Ceramatec Inc, Salt Lake City, Utah, USA.

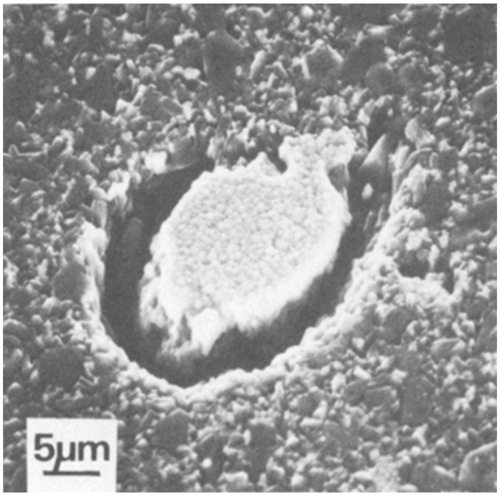


Figure 1 Presence of ZrO_2 agglomerates in composites leads to "void-like" microstructural defects (light phase is ZrO_2).

Strength measurements were performed in four-point bending (outer span 25.4 mm and inner span 12.7 mm) on rectangular specimens of cross-section approximately 3 mm × 4 mm. These specimens had been diamond machined from the square billets and the edges were chamfered to prevent failure from corner cracks. The failure origins were subsequently identified on the SEM.

3. Results and discussion

In previous work, it was established that it is important to remove ZrO_2 agglomerates from the starting powder. As shown in Fig. 1, these agglomerates densify more rapidly than the surrounding matrix and give rise to "void-like", microstructural defects. No such defects were observed around large β''-Al_2O_3 grains or agglomerates and thus, as pointed out in Section 1, it may not be necessary to remove agglomerates from the β''-Al_2O_3 powder, particularly if it gives rise to increase in ionic resistivity. In order to optimize the fabrication procedure a set of β''-Al_2O_3/15 vol % t-ZrO_2 composites were made in which the β''-Al_2O_3 powder was sedimented for various times, such that the largest particle would be less than a given size. The ionic resistivities of these materials are shown in Table I and it is clear that sedimentation of the β''-Al_2O_3 powder gives rise to increases in ionic resistivity. Fig. 2 compares the microstructure for the extremes of the sedimented series and the presence of large β''-Al_2O_3 grains was clear for the materials with short sedimentation times. For the rest of the study, it

TABLE I Effect of removing agglomerates from β''-Al_2O_3 powder on ionic resistivity

β''-Al_2O_3 particle size (μm)	Ionic resistivity, 300° C (Ωcm)
As-received	8.5
< 10*	8.5
< 5*	9.9
< 2*	10.9
< 1*	11.9

*Sedimented assuming Stokes Law is valid; ZrO_2 < 1 μm.

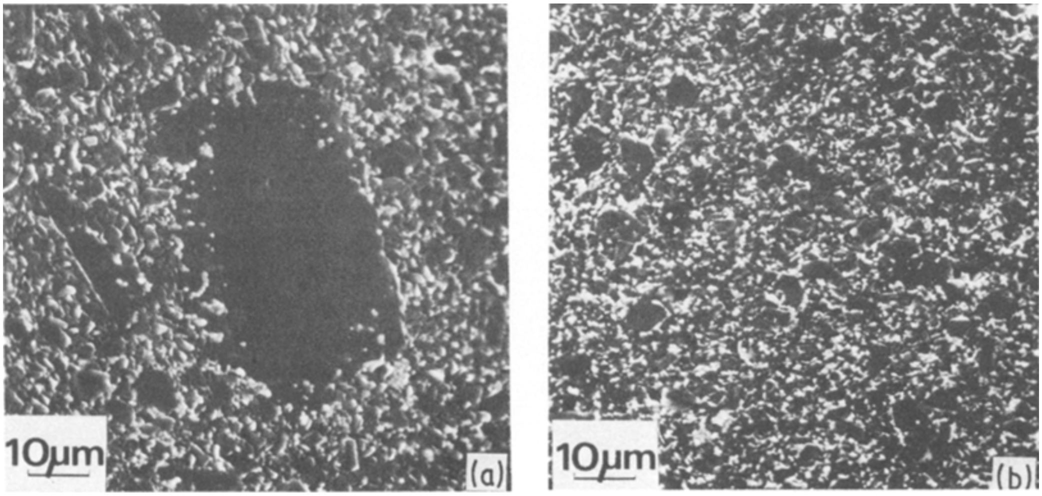


Figure 2 Comparison of microstructures of β''-Al_2O_3/15 vol % t-ZrO_2 in which (a) no agglomerates were removed from β''-Al_2O_3 powder and (b) in which agglomerates nominally < 1 μm were removed (light phase is ZrO_2).

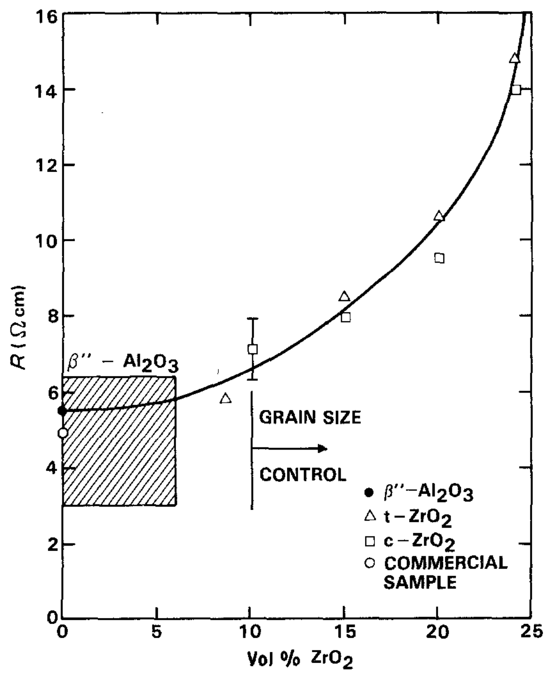


Figure 3 Ionic resistivity (300° C) for β''-Al_2O_3/ZrO_2 composites as a function of volume fraction t-ZrO_2 or c-ZrO_2.

TABLE II Relative amounts of β''-Al_2O_3 and β'-Al_2O_3 in composites

Vol % t-ZrO_2	$f'(\beta)$	Vol % c-ZrO_2	$f'(\beta)$
0	< 0.01		
8.7	0.05	10	0.02
15	0.08	15	0.04
20	0.17	20	0.03
25	0.25	25	0.05

was decided not to sediment the β''-Al_2O_3 slip prior to casting.

The ionic resistivity measurements at 300° C for the composites containing t-ZrO_2 or c-ZrO_2 are shown in Fig. 3. The influence of the ZrO_2 additions is very similar for both sets of composites. The dispersed ZrO_2 is expected to act as an inert phase in terms of sodium ion conduction and thus will tend to block the ionic conduction process. Comparison of the data with effective medium percolation theory [13], assuming the ionic conductivity for sodium in ZrO_2 is negligible compared to β''-Al_2O_3, indicates the increase in resistivity with the addition of ZrO_2 is more rapid than expected for a randomly dispersed mixture of the two phases. Part of the explanation may be the change in grain size of the β''-Al_2O_3 as the volume fraction of ZrO_2 is increased. As pointed out previously [6], the addition of 10 vol % or greater of ZrO_2 is effective in eliminating exaggerated grain growth of the β'' phase. This decreasing grain size is expected to increase the grain-boundary contribution to the bulk ionic resistivity. For example, Youngblood *et al.* [14] have shown that changing the grain size of β''-Al_2O_3 from 100 to 2 μm increases the ionic resistivity by a factor of ~ 1.6. X-ray diffraction of the two sets of composites showed that in addition to ZrO_2 and β''-Al_2O_3, β-Al_2O_3 was present. This phase can also increase ionic resistivity [14] and the values for $f'(\beta)$ are shown in Table II. It is interesting to note that the amount of β-Al_2O_3 increases with the amount of ZrO_2 added and may indicate there is some chemical reaction between the β''-Al_2O_3 and the ZrO_2. For the c-ZrO_2 series, however, the amount of β-Al_2O_3 is rather low and is thus probably not a major factor in increasing the resistivity. Youngblood *et al.* [14] used an index $f(\beta)$ to describe the influence of the β-Al_2O_3 on resistivity. Unfortunately, the diffraction peaks used in their assessment cannot be easily used here, as there is an overlap of one of their peaks with a c-ZrO_2 or t-ZrO_2 peak. A preliminary assessment indicates that their parameter $f(\beta)$ will tend to be higher than $f'(\beta)$ for a given amount of β-Al_2O_3. Even when making an approximate correction to our parameter $f'(\beta)$, it does not appear that the presence of the β-Al_2O_3 in our composites is a major factor in increasing resistivity, when compared to their results [14]. A final possibility is that chemical interaction may be occurring between the ZrO_2 and the β''-Al_2O_3 or other phases may be present at grain boundaries, which could block conduction. Further work will be needed, including electron microscopy, before the various contributions can be distinguished.

Fig. 4 shows the ionic conductivity measurements of selected β''-Al_2O_3/t-ZrO_2 composites and are compared with the data for a commercial β''-Al_2O_3 disc. The conductivity behaviour of the commercial disc is in good agreement with the literature both in terms of absolute conductivity and the activation energy (~ 5.2 kcal mol^{-1}) [14]. The addition of t-ZrO_2 does not significantly influence the conduction process in terms of activation energy, only in the absolute value of ionic conductivity.

The microstructure of a 15 vol % t-ZrO_2 composite is compared in Fig. 5 with that of single

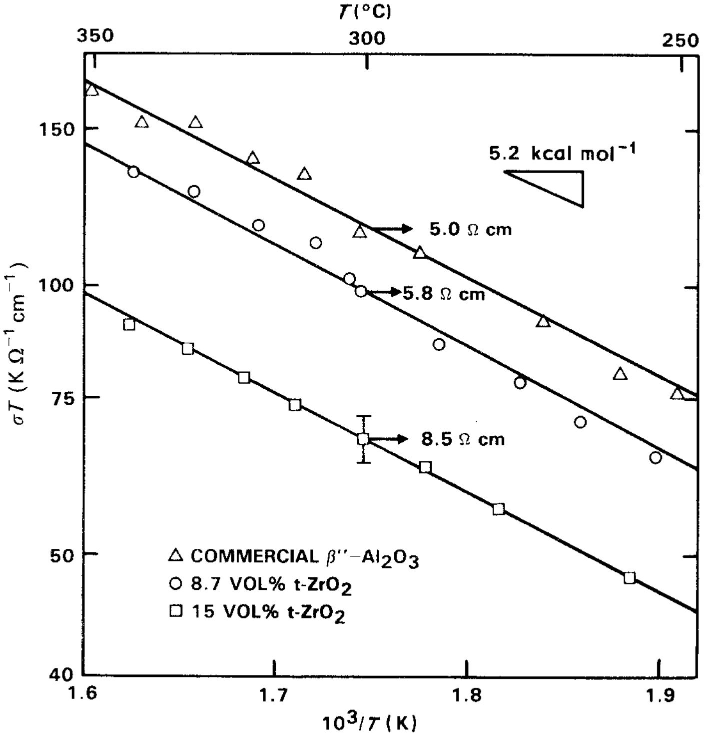


Figure 4 Ionic resistivity as a function of temperature for commercial β''-Al_2O_3 compared with composites containing t-ZrO_2.

phase β''-Al_2O_3 and a 15 vol % c-ZrO_2 composite all fabricated in the same way. There are several items to note. First, as indicated earlier, the addition of ZrO_2, either cubic or tetragonal eliminates the presence of the abnormally large grains that are often found in the single phase material. As suggested previously [6], this effect is important in terms of strengthening as it eliminates flaw populations associated with these large grains, especially as they are known to cleave easily [15]. The microstructure of the c-ZrO_2 and t-ZrO_2 composite were similar, although it was noted that the grain size of the c-ZrO_2 phase was larger than that of the t-ZrO_2 phase at a given volume fraction. The origin of the difference is not clear but it is not expected to significantly influence the mechanical property measurements.

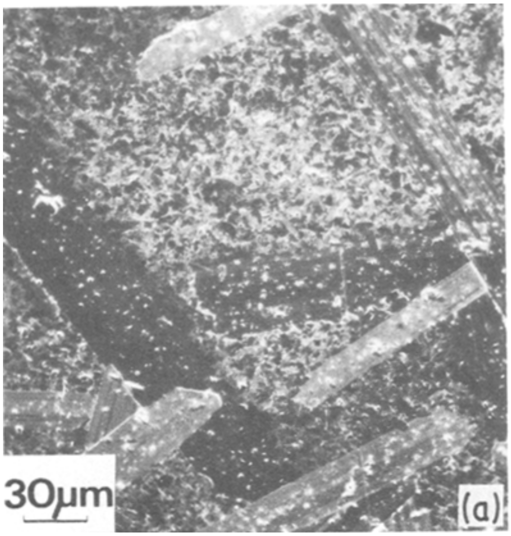
A comparison of the K_{IC} values for the two composite series are shown in Table III. The values for the t-ZrO_2 composites are similar to those reported earlier [6]. It was found that the t-ZrO_2 composites are significantly higher in fracture toughness than the c-ZrO_2 series and this difference is ascribed to transformation toughening.

As indicated earlier, two strengthening mechanisms are feasible in these composites, that is, a decrease in the critical flaw size as a result of grain growth control and the change in K_{IC}. This is best understood in the terms of the relationship between K_{IC} and strength (S), i.e. $K_{IC} = YSa^{\frac{1}{2}}$, where Y is a constant that depends on the loading and crack geometry and a is the size of the critical flaw. If we assume, first that there is no change in flaw size when adding ZrO_2 to β''-Al_2O_3, it is possible to predict the strengthening due to changes only in K_{IC}. In order to accomplish this, we need the strength (S_0) and K_{IC}^0 of single phase β''-Al_2O_3 that was fabricated in the same way as the composite series. These values were 147 MPa and 3.0 MPa m$^{\frac{1}{2}}$, respectively. The predicted strength of the composites assuming no change in flaw size is therefore simply given by

$$S_p = S_0 K_{IC}/K_{IC}^0 \qquad (1)$$

TABLE III Comparison of K_{IC} for β''-Al_2O_3 composites containing either c-ZrO_2 or t-ZrO_2

Vol % ZrO_2	K_{IC} (MPa m$^{1/2}$)	
	c-ZrO_2	t-ZrO_2
0	3.0	3.0
10	3.5	3.3
15	3.2	4.1
20	3.3	4.1
25	3.9	4.4



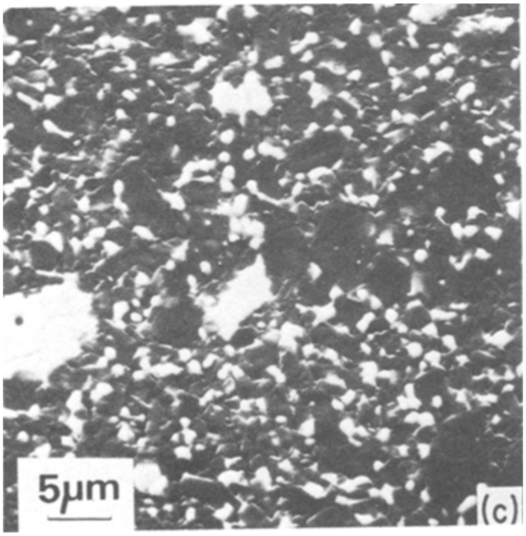


Figure 5 Microstructural comparison for (a) single phase β''-Al_2O_3, with (b) 15 vol % t-ZrO_2, and (c) 15 vol % c-ZrO_2 composites, showing elimination of large β'' grains. Micrographs (b) and (c) obtained in back-scattered mode (SEM); light phase is ZrO_2.

Using the data from Table II, the predicted and measured strengths of 15 vol % ZrO_2 composites are given in Table IV. It was found that the increase in K_{IC} for either composite predicted strengths much less than the measured values. It is therefore concluded that the major strengthening mechanism for these composites is the reduction in critical flaw size and this reduction is in turn ascribed to the control of grain growth of the β''-Al_2O_3 by the ZrO_2 additions. It is important to note therefore that as even the c-ZrO_2 additives increase strength in these materials, that there exists the possibility of selecting other compatible phases as additions to β''-Al_2O_3 and obtaining improved strengths. Alternatively, techniques that could control exaggerated grain growth in the single phase material, e.g. fast firing, would also improve strength [15]. In this latter case, the contribution to strength of transformation toughening would then become more significant. The measured strengths for the transformation-toughened materials were somewhat lower than measured previously [6]. Observation of the failure origins on the SEM for both sets of composites indicated that failure was occurring from two sources. The origins were either voids or two phase agglomerates (Figs. 6 and 7). The source of these microstructural defects were postulated to be organic debris picked up either in the processing or present in the as-received powders, while the agglomerates could be a result of the slip drying on the side of the container and subsequently being entrapped in the slip. Improvements in processing should allow higher

TABLE IV Comparison of measured average strengths of β''-Al_2O_3/ZrO_2 composites with that predicted from K_{IC} measurements

	Predicted strength* (MPa)	Measured strength (MPa)
15 vol % t-ZrO_2	201	335
15 vol % c-ZrO_2	157	226

*Assuming no change in flaw size.

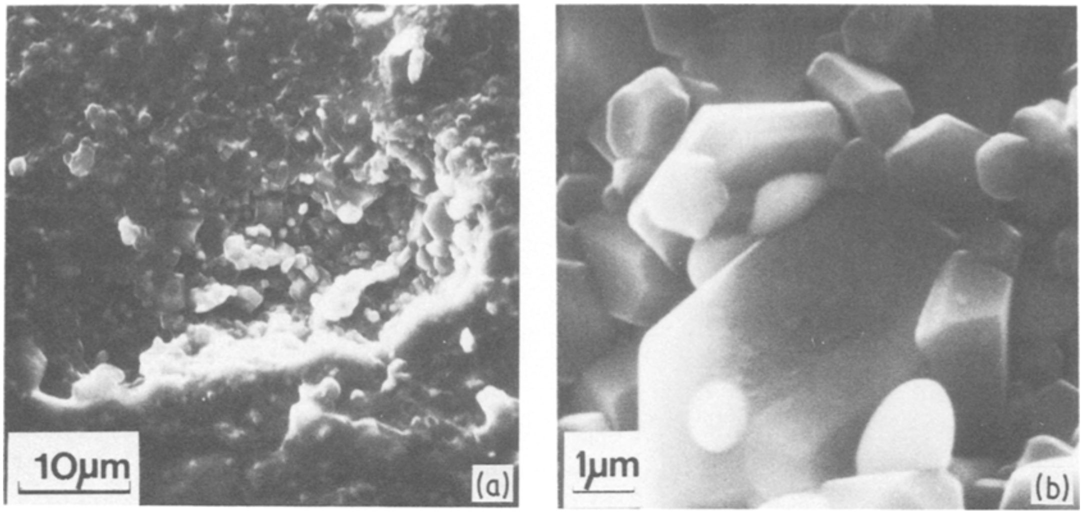


Figure 6 Failure originating from a void (left). The inside surface of these origins is etched (right), indicating it was a free surface at the firing temperature.

strengths to be obtained, at least in line with those measured earlier [6].

In summary, it was found for significant increases in fracture toughness and strength, t-ZrO_2 is more effective than c-ZrO_2. In particular, additions of t-ZrO_2 between 10 and 20 vol % appear optimum in terms of improved mechanical properties and microstructural control, while giving materials with ionic resistivities (300° C) between 6 and 10 Ωcm.

4. Conclusions

1. Although in the fabrication of β''-Al_2O_3/ZrO_2 it is important to remove ZrO_2 agglomerates, it was found to be unnecessary to remove β''-Al_2O_3 agglomerates, particularly as this gives rise to higher ionic conductivity and as no defects were observed in the vicinity of large β''-Al_2O_3 grains.

2. In addition to the dependence on the particle size of the β''-Al_2O_3 starting powder, the ionic conductivity depends on the volume fraction of ZrO_2 in the composites. The change in conductivity is greater than expected for a random mixture of the two phases. The decreasing grain size of the β''-Al_2O_3 with additions of ZrO_2 could be involved with this difference. The activation energy for the conduction process is not significantly changed by the addition of ZrO_2 in the temperature range 250 to 350° C.

3. The fracture toughness of composites containing t-ZrO_2 was found to be significantly higher than those containing c-ZrO_2 and this difference was ascribed to transformation toughening.

4. Additions of t-ZrO_2 or c-ZrO_2 both gave rise to strengthening of the β''-Al_2O_3, when compared to the single phase material fabricated in the same way. For both sets of composites, the major strengthening mechanism was found to be reduction in the critical flaw size. This is a result of the grain growth control of β''-Al_2O_3 by the ZrO_2 additions ($\geqslant 10$ vol %). This indicates

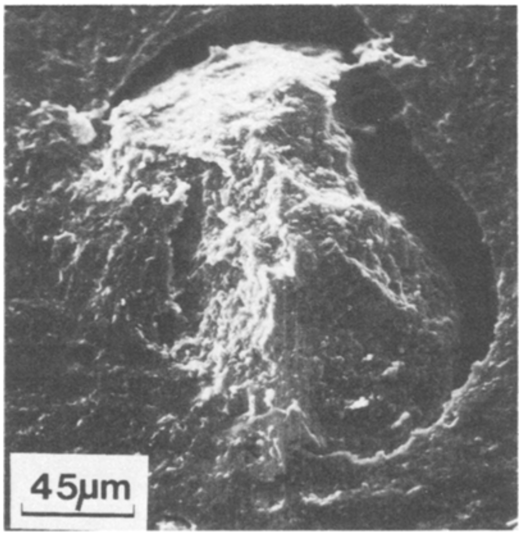


Figure 7 Failure originating from a mixed β''-Al_2O_3/ZrO_2 agglomerate.

that additions of other compatible phases could be used to strengthen β''-Al_2O_3.

5. For maximum increases in fracture toughness and strength, grain growth control and ionic resistivities $< 10\ \Omega$cm, additions of t-ZrO_2 between 10 and 20 vol % are necessary.

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